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# Dielectric properties of the multicomponent PZT-type solid solution<sup>\*</sup>

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**Abstract.** In this paper the multicomponent PZT-type solid solution doped by barium, calcium, strontium, bismuth and germanium with composition:  $\text{Pb}_{0.975}\text{Ba}_{0.01}\text{Ca}_{0.01}\text{Sr}_{0.005}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3 + 1.4 \text{ wt.}\% \text{Bi}_2\text{O}_3 + 0.3 \text{ wt.}\% \text{GeO}$  obtained by hot uniaxial pressing method is described. The results of structural, dielectric, ferroelectric and electromechanical studies of these ceramics are presented. It has been stated that introduction to the basic composition PZT admixtures of the barium, calcium, strontium, bismuth and germanium has a positive effect on the electro-physic parameters of obtained ceramic samples. This material has good microstructure, with high value of the dielectric permittivity (with the high temperature of phase transition) as well as low dielectric losses. It allows considering this material as elements for low frequency and high temperature electromechanical transducers.

## 1 Introduction

Investigated material PZT-type with perovskite structure belongs to the family of multicomponent solid solutions with general formula  $(1-x)\text{PbZrO}_3-x\text{PbTiO}_3$  [1–4]. At room temperature the PZT binary phase diagram can be roughly described in three areas. The rhombohedral Zr-rich region is separated from the tetragonal Ti-rich one by a morphotropic phase boundary (noted MPB) in which the two phases coexist [5,6]. Wide isomorphism of this solid solution enables to substitute appropriate cations in the basic place of Pb, Zr and Ti [7]. An appropriate selection of the composition (from rhombohedral, tetragonal phases or morphotropy area), opportunely doping the basic composition and conditions of a technology ceramic powders and samples allows obtaining the materials, which can be used widely in different types of piezoelectric transducers, electronic sensors, actuators, resonators and filters for microelectronics and micromechatronics [8–10]. For PZT-type ceramics from morphotropic region (first of all  $\text{Zr}/\text{Ti} = 0.52/0.48$ ) the physical parameters of ceramics are usually extremely high or extremely low what is very important for applications [11]. To improve piezoelectric and other properties, the base composition PZT is admixed [12,13]. The addition of the third, the fourth and the fifth components, the piezoelectric properties can be adjusted over a wide range [14]. The multicomponent

PZT-type solid solutions are widely used in electronic smart applications (transformers, sensors and actuators, accelerometers, transducers, speakers, electric resonators as well as gas igniters) [11]. On the basis of ferroelectric and ferrimagnetic powders may be obtained composite materials for numerous applications including magnetic field sensors, filters, memory devices, transducers, switches, waveguides, phase invertors [15,16].

The main aim of this work was to obtain multicomponent  $\text{Pb}_{0.975}\text{Ba}_{0.01}\text{Ca}_{0.01}\text{Sr}_{0.005}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3 + 1.4 \text{ wt.}\% \text{Bi}_2\text{O}_3 + 0.3 \text{ wt.}\% \text{GeO}$  ceramics using hot uniaxial pressing method and research basic electrophysical properties.

## 2 Experiment

The obtained and investigated multicomponent material with mainly chemical composition:  $\text{Pb}_{0.975}\text{Ba}_{0.01}\text{Ca}_{0.01}\text{Sr}_{0.005}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$  doped by bismuth (1.4 wt.%  $\text{Bi}_2\text{O}_3$ ) and by germanium (0.3 wt.%  $\text{GeO}$ ). The initial constituents for obtaining PZT type powder were commercially available oxides:  $\text{PbO}$  (99.9%),  $\text{ZrO}_2$  (99.5%),  $\text{TiO}_2$  (99.99%),  $\text{Bi}_2\text{O}_3$  (99.999%),  $\text{GeO}_2$  (99.99%) as well as carbonates: barium  $\text{BaCO}_3$  (99.99%), calcium  $\text{CaCO}_3$  (99.99%) and strontium  $\text{SrCO}_3$  (99.99%). In order to keep a designed lead content in the powder, an excess of 5.0 wt.%  $\text{PbO}$  was introduced into the stoichiometric mixture of the relevant oxides. The constituent components were mixed using Fritsch planetary ball mill for 8 h in ethyl alcohol medium.

The main component of the composite powder was pressed into pellets and synthesized by classical method in solid phase at temperature  $T_{\text{synth}} = 850^\circ\text{C}$  for time

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$t_{synth} = 4$  h. The synthesis conditions were selected on the basis of differential thermal analysis DTA and TG using a Q-1500D derivatograph in the temperature range from 20 °C to 1030 °C (these studies not presented here). Final densification (sintering) of the synthesized powder was carried out by hot uniaxial pressing method using following technological conditions:  $T_{sint} = 1170$  °C,  $t_{sint} = 1$  h,  $p_{sint} = 10$  MPa. In last step of technology the silver paste electrodes have been put onto every surface of sample using the burning method.

The X-ray tests at room temperature were performed using the diffractometer Phillips X'Pert APD (Cu-K $\alpha$  radiation). Microstructure and EDS (Energy Dispersive Spectrometry) tests were carried out using a scanning microscope HITACHI S-4700. Dielectric and impedance measurements were performed using QuadTech 1920 LCR meter for a cycle of heating (at frequencies of the measurement field from 0.02 kHz to 1.0 MHz). Dielectric hysteresis loops  $P$ - $E$  were investigated using Sawyer-Tower circuit and a Matsusada Inc. Heops-5B6 precision high voltage amplifier. Electromechanical measurements were carried out using an optical displacement meter (Philtec Inc., D63) and Matsusada Inc. HEOPS-5B6 precision high voltage amplifier. Data were stored on a computer disc using an A/D, D/A transducer card and LabView computer program. Measurements of direct current electric conduction were performed in the temperature range from 20 °C to 450 °C using a 6517B Keithley electrometer (high resistance meter). Ceramic samples were polarized by low temperature method using a Matsusada Precision Inc. HEOPS-5B6 high voltage amplifier under the following conditions: poling temperature  $T_{pol} = 130$  °C, poling field  $E_{pol} = 35$  kV/cm, poling time  $t_{pol} = 1$  h. Examinations of the piezoelectric parameters were carried out using the resonance-antiresonance method in the frequency range of the measuring field from 20 Hz to 1 MHz.

### 3 Results and discussion

XRD data of the PZT type ceramics obtained at room temperature is presented in Figure 1. It is seen that at room temperature this material is perovskite-type, without foreign (non-perovskite) pyrochlore phase. The best fit to the measured data was obtained with the pattern 01-072-7167 (tetragonal crystal system, with space group  $P4mm$  and unit cell parameters:  $a = 4.0429$  Å,  $b = 4.0429$  Å,  $c = 0.1315$  Å).

Figure 2 shows the SEM image of the microstructure of the multicomponent PZT type ceramics. The microstructure of the PZT type ceramics shows densely packed fine grains, and fracture takes mainly along the grain boundary but as well as through the grains. The grains (with average grains size  $r < 3$  μm) have regular shape and boundary layer between grains is imprecisely determined.

Figure 3 shows the EDS tests (Energy Dispersive Spectrometry) of the analyzed ceramics (the EDS included measurement of ten randomly selected areas of the sample fractures). The analysis confirmed the assumed chemical composition of the multicomponent PZT type ceramics.

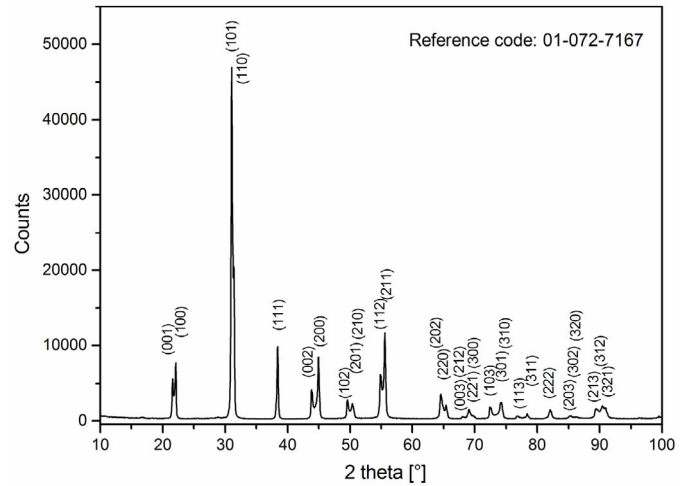


Fig. 1. X-ray patterns of the PZT-type ceramic powders.

In the graph of the  $\ln \sigma_{DC}(1/T)$  for PZT-type ceramics (Fig. 4) there are three characteristic inflection points where there is a change in the  $E_{Act}$  activation energy. Change the value of the  $E_{Act}$  is visible in the phase transition too. Activation energies were calculated according to the Arrhenius law:

$$\sigma_{DC} = \sigma_0 e^{-\frac{E_{Act}}{k_B T}} \quad (1)$$

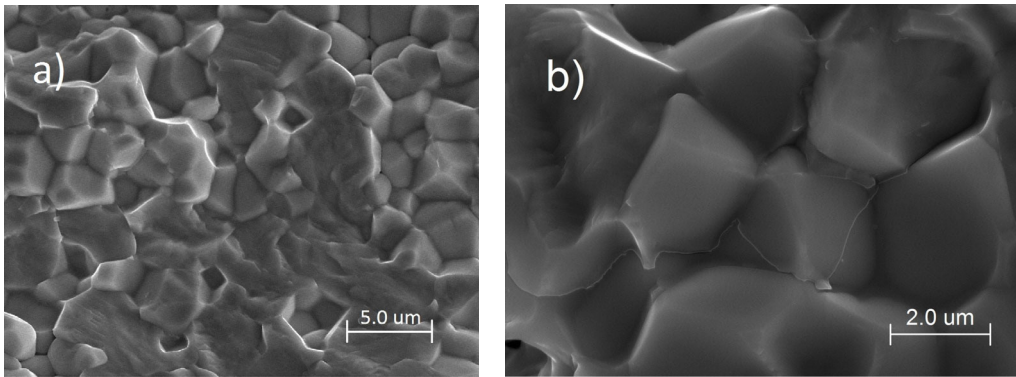
where:  $k_B$  – Boltzmann constant,  $E_{Act}$  – activation energy,  $T$  – absolute temperature.

Like most materials with perovskite structure also for the obtained ceramic samples there is an increase in value of activation energy  $E_{Act}$  in high temperatures (Fig. 4, Tab. 1).

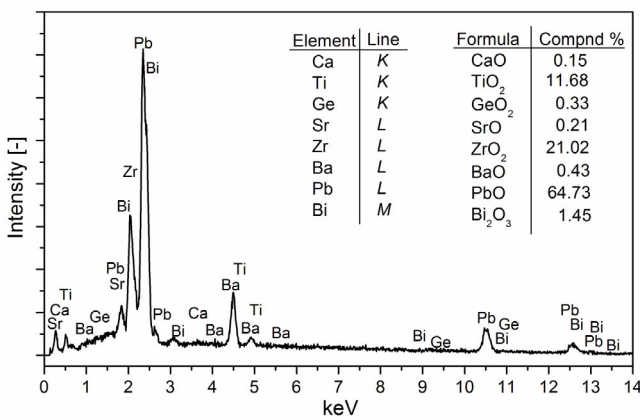
Temperature dependences of the dielectric permittivity are presented in Figure 5. Multicomponent PZT-type exhibits a sharp phase transition from the ferroelectric phase to the paraelectric phase. When the values of frequency measurement field increases the values of dielectric permittivity decreases. The increase the frequency measurement field does not induce phase transition temperature shifts (see plot insert in Fig. 5).

For the PZT-type in the temperature range from room temperature to the about 300 °C temperature (for 1 kHz) the values of dielectric losses are low (Fig. 6). Above the temperature phase transition the dielectric losses strongly increases (which is associated with increase electric conductivity). The insert in Figure 6 shows the image of temperature dependencies of the dielectric losses for all measurement frequency. Generally, in the whole of the measuring area, when the frequency measurement field increases, the dielectric losses decrease. Above 50 kHz is a change in this trend and dielectric losses in the measurement area increase. The dielectric properties (for 1 kHz) of the obtained ceramic are presented in Table 1.

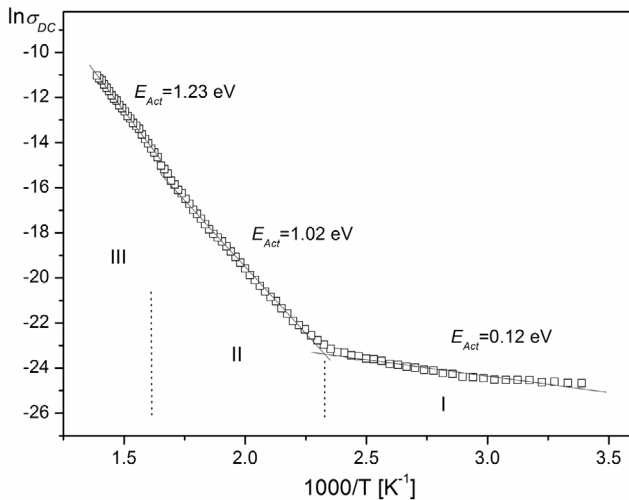
Hysteresis  $P$ - $E$  loops for the PZT type ceramics are very wide, with good saturated already for the electric field  $E_{\sim} = 3.0$  kV/cm for  $f = 1$  Hz (Fig. 7). At room temperature (for 4.0 kV/cm) this material has high values of spontaneous polarization and residual polarization.



**Fig. 2.** SEM images of the microstructures multicomponent PZT-type ceramics: (a) magnification  $\times 5000$ , (b) magnification  $\times 15000$ .



**Fig. 3.** EDS study for the multicomponent PZT-type ceramics.



**Fig. 4.** Temperature dependence of the electrical conductivity for the PZT type ceramics.

The values of spontaneous polarization  $P_S$ , residual polarization  $P_r$  and coercive field  $E_C$  (for  $f = 1$  Hz) are summarized in Table 1.

Figure 8 shows hysteresis loops at room temperature obtained for various frequencies of measurement field. The  $P$ - $E$  hysteresis loops (for  $E_{\sim} = 4.0$  kV/cm) are slightly

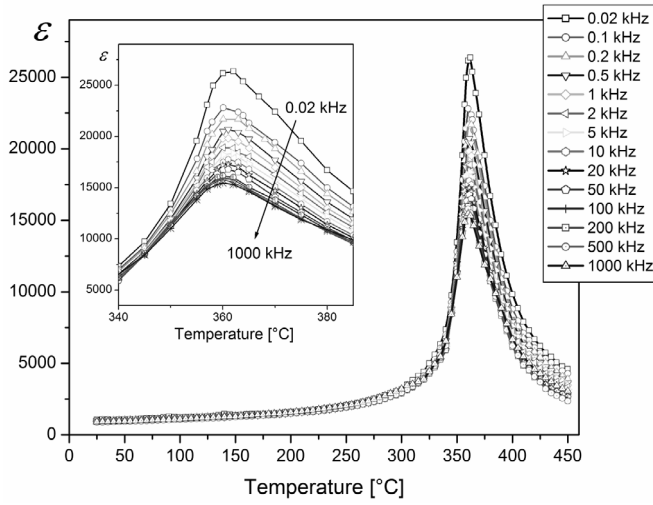
**Table 1.** Parameters of the PZT-type ceramics (dielectric properties for  $\nu = 1$  kHz).

	Sample
$\rho$ [g/cm <sup>3</sup> ]	7.43
$T_m$ [°C]	360
$\epsilon_r$	1000
$\epsilon_m$	19.930
$\tan \delta$ at $T_r$	0.031
$\tan \delta$ at $T_m$	0.095
$E_{Act}$ [eV] at I area	0.12
$E_{Act}$ [eV] at II area	1.02
$E_{Act}$ [eV] at III area	1.23
$P_S$ [ $\mu$ C/cm <sup>2</sup> ] at $T_r$ (for $E = 4$ kV/cm)	28.52
$P_R$ [ $\mu$ C/cm <sup>2</sup> ] at $T_r$ (for $E = 4$ kV/cm)	26.01
$E_C$ [kV/mm] at $T_r$ (for $E = 4$ kV/cm)	1.84
$d_{33}$ [C/N] $\times 10^{12}$	250
$S_{rest}$ [%]	0.13
$S_{max}$ [%]	0.27
$H_S$ [%]	24.07
$k_p$	0.43
$-d_{31}$ [C/N] $\times 10^{12}$	102
$V_r$ [m/s]	1810
$g_{31}$ [Vm/N] $\times 10^3$	10.08

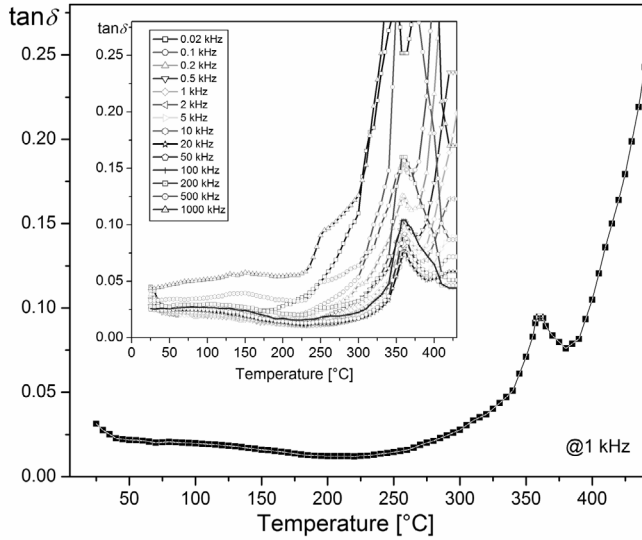
less dependent on the frequency. The  $P$ - $E$  hysteresis loops are very wide and together with the increase of the measuring field's frequency, the values of maximum of polarization slightly decreased while the values of coercive field increase.

Temperature hysteresis  $P$ - $E$  loops for the PZT type ceramics (obtained for 4.0 kV/mm) are presented in Figure 9. The values of spontaneous polarization  $P_S$  and residual polarization  $P_r$  decrease with increasing temperature. Temperature increase causes a decrease in value of coercive field  $E_C$  from 1.87 kV/mm (for 22 °C) to 0.98 kV/mm (for 150 °C). At higher temperatures the electric hysteresis loops have high saturation and become narrower.





**Fig. 5.** Temperature dependencies of the relative dielectric permittivity properties for the PZT type ceramics.

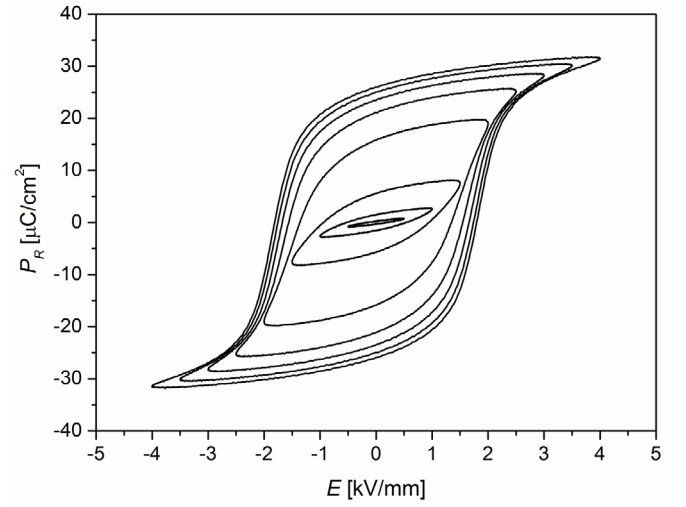


**Fig. 6.** Temperature dependencies of the dielectric losses for the PZT type ceramics.

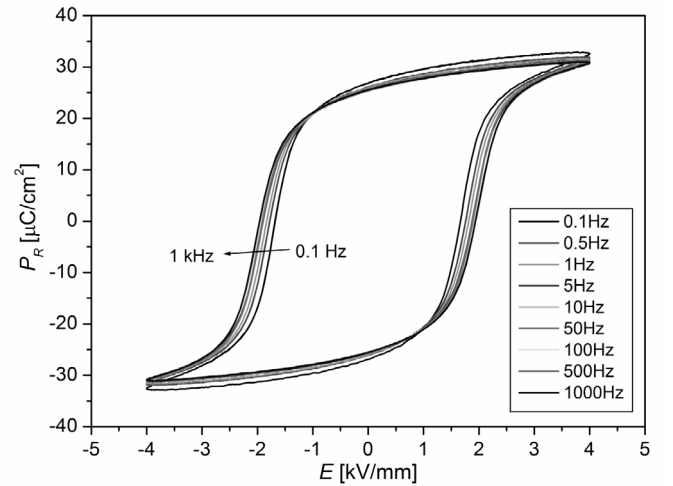
Figure 10 shows the bipolar electric field-induced strain loops for the PZT-type ceramics. The normalized strain coefficient ( $d_{33} = S/E$ ) was measured under 0.5 kV/mm electric field and frequency 1 Hz (Tab. 1). The electromechanic loops take on the butterfly characteristic shape, typical for piezoelectric materials (linear dependency) and demonstrate good value of residual strain  $S_{rest}$  and strain hysteresis coefficient  $H_S$  (Tab. 1). The strain hysteresis coefficient was calculated according to the formula [13]:

$$H_S = (H_{half}/S_{max}) \times 100\% \quad (2)$$

where:  $H_{half}$  – the hysteresis of etrains (the difference between maximum and minimum strain for the half of the maximum electric field [%]),  $S_{max}$  – strain for the maximum applied electric field [%].



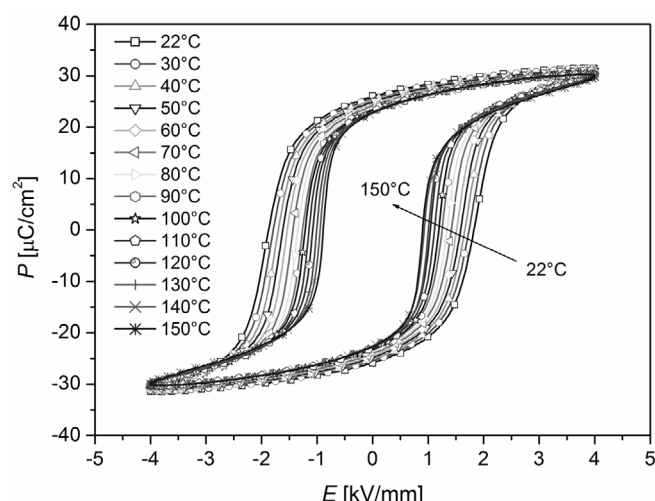
**Fig. 7.** Influence an electrical filed on the saturation hysteresis  $P$ - $E$  loops for PZT type ceramics.



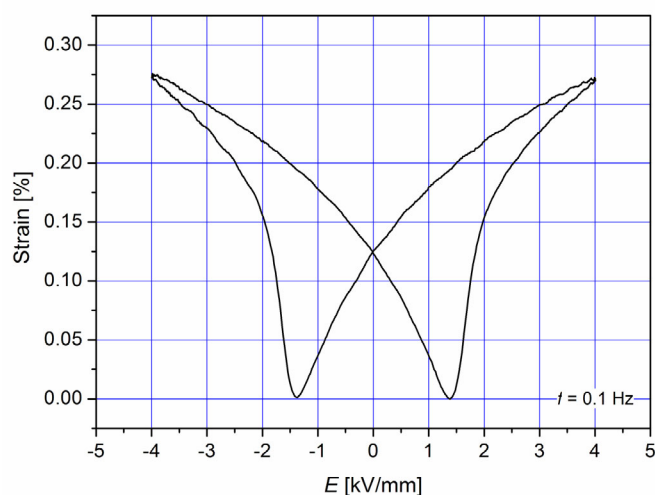
**Fig. 8.** Influence the measuring field's frequency on the hysteresis  $P$ - $E$  loops for PZT type ceramics.

The PZT-type samples were polarized using high-voltage method under the following conditions: poling temperature  $T_{pol} = 130$  °C, poling field  $E_{pol} = 35$  kV/cm, poling time  $t_{pol} = 1$  h. This material has average values of piezoelectric parameters (measured by resonance-antiresonance method): the electromechanical coupling coefficient  $k_p \sim 0.43$  and the piezoelectric modulus  $d_{31} \sim 102 \times 10^{-12}$  C/N,  $g_{31} \sim 10.08 \times 10^{-12}$  [Vm/N].

Multicomponent  $\text{Pb}_{0.975}\text{Ba}_{0.01}\text{Ca}_{0.01}\text{Sr}_{0.005}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3 + 1.4$  wt.%  $\text{Bi}_2\text{O}_3 + 0.3$  wt.%  $\text{GeO}$  solid solutions, belongs to the morphotropic area. Introduced into the basic composition of the dopant barium  $\text{Ba}^{2+}$ , strontium  $\text{Sr}^{2+}$  and calcium  $\text{Ca}^{2+}$  ions (placed in A positions of elementary cell) lead to the improve of the dielectric properties (increase of the value of dielectric permittivity), while the admixture of bismuth  $\text{Bi}^{3+}$  reduces the ferroelectric hardness of the ceramic samples. Introduced into the basic composition the admixture of germanium



**Fig. 9.**  $P$ - $E$  hysteresis loops (temperatures from 20 °C to 150 °C): (a) and the temperature dependences of  $P_r$ ,  $P_s$  and  $E_C$ , (b) for obtained PZT type ceramics.



**Fig. 10.** Strain vs. electric field loops for the PZT-type ceramics measured at room temperature, under electric field 4 kV/mm and frequency of 0.1 Hz.

$\text{Ge}^{2+}$  reduces the temperature of sintering and increases the stability of the electro-physical parameters.

## 4 Conclusions

In this paper the multicomponent  $\text{Pb}_{0.975}\text{Ba}_{0.01}\text{Ca}_{0.01}\text{Sr}_{0.005}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3 + 1.4 \text{ wt.}\% \text{ Bi}_2\text{O}_3 + 0.3 \text{ wt.}\% \text{ GeO}$  solid solution (from the morphotropic area) has been obtained using the hot uniaxial pressing method. The microstructure of obtained ceramics shows fine-grained and well crystallized grains. These ceramics have acceptable properties and acceptable complex

of parameters (high values of dielectric permittivity, low dielectric losses, good electromechanic and piezoelectric parameters). The electric hysteresis loops are very wide and at higher temperatures they have high saturation and become narrower.

Choosing appropriate composition (for examples with morphotropy area) as well as appropriate methods and technological conditions it is possible to obtain ceramic materials for different types of electromechanical, electroacoustic, pyroelectric and piezoelectric transducers, sensors and memory elements to application in microelectronics and micromechatronics. The high value of electric permittivity allows the use of this material as low-frequency transducers as well as the high temperature of phase transition allows the use of such materials for high temperature transducers.

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